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| Title: | Micro X-ray Fluorescence for Spatially Resolved Elemental Materials Characterization |
| Author(s): | Havrilla, George J |
| Intended for: | Invited seminar at NIST Boulder |

# Micro X-ray Fluorescence for Spatially Resolved Elemental Materials Characterization

George J. Havrilla
NIST Boulder
November 8, 2012

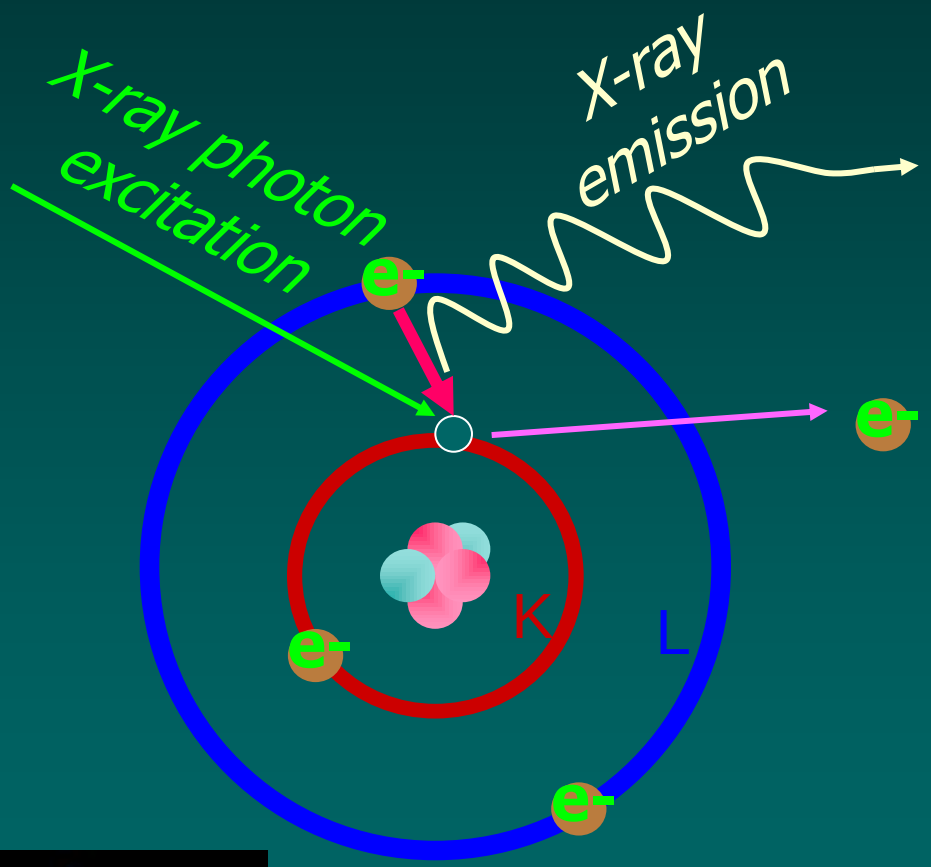


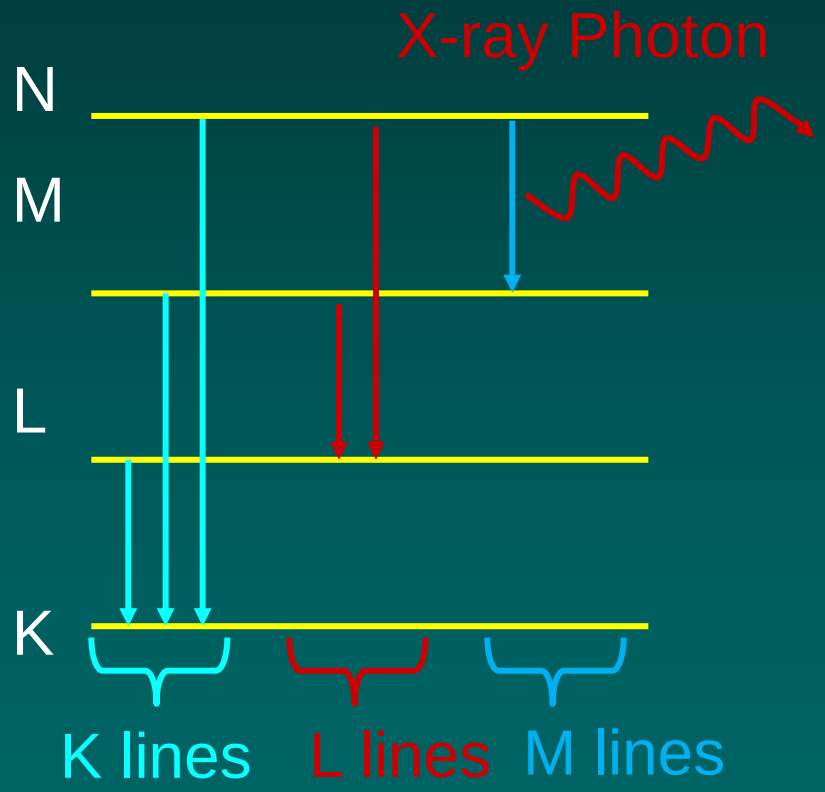
LAUR 12-XXXXX

# Overview

- Introduction – XRF and elemental imaging
- Experimental - optics
- Instrumentation
  - Polycapillary – 2D EDAX Eagle III
  - DCC – 2D hiRX R&D instrument
  - Polycapillary – 3D R&D instrument
- Matrices – simple to complex
- Summary
- Future Directions

# XRF Process


X-ray photon excitation
X-ray emission
e-
e-
e-
e-
K
L

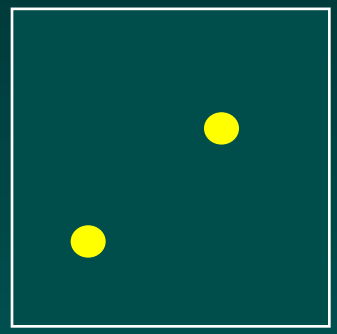

X-ray Photon
N
M
L
K
K lines
L lines
M lines

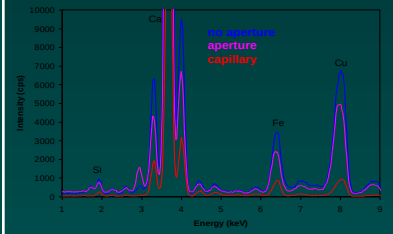
# MXRF

- Spatially resolved elemental analysis
- Spatial resolution down to 10 micrometers with commercial X-ray optics
- Limited sensitivity due to energy filtering by polycapillary optic
- Multi-element mapping
- Commercial laboratory based instrumentation

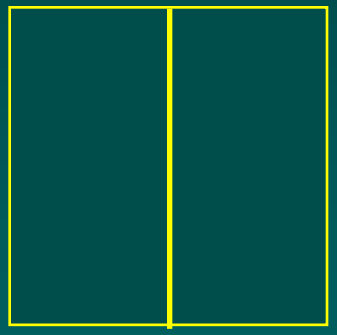
# MXRF Capabilities

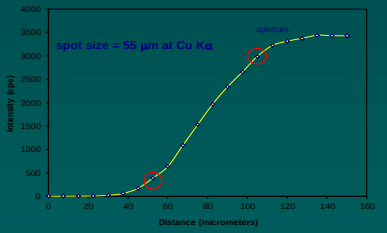
- Single point analysis, spatially resolved, quantitative



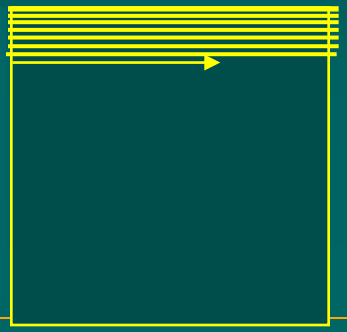


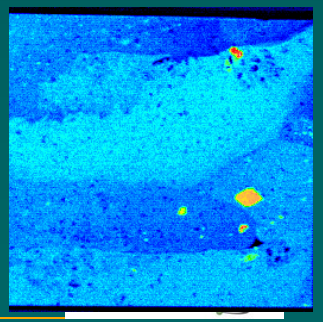

- Line scans - concentration gradients, qualitative






- Maps or elemental imaging - large area heterogeneity, PIWTA, qual and quant





# Elemental Imaging

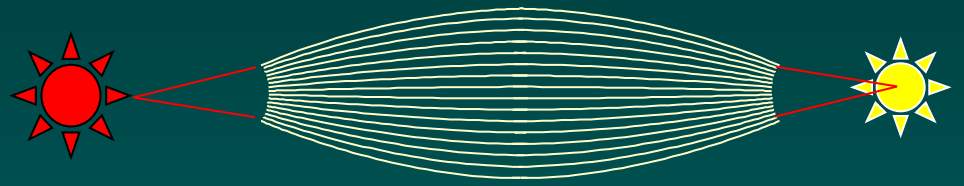
- Spatially resolved elemental characterization
- Single point spectra, line scans and elemental maps/elemental imaging
- X-ray optics need to be selected for the application
  - Spatial resolution
  - Sensitivity
  - Spectral range/resolution

# Optics

- Polycapillary 2D – EDXRF EDAX Eagle III MXRF instrument, 40 kV, 1 mA, Rh, ~50 micrometer spot size
- DCC (doubly curved crystal) 2D – research instrument, 50 kV, 1 mA, Rh, 200 μm
- Polycapillary 3D – research instrument, 50 kV, 0.5 mA, Ag, 30 x 30 x 60 μm

# Polycapillary optics

- Shaped bundle of glass capillaries
- Polychromatic
- High X-ray intensity
- High sensitivity
- Compromised spatial selectivity
- Rapid data collection

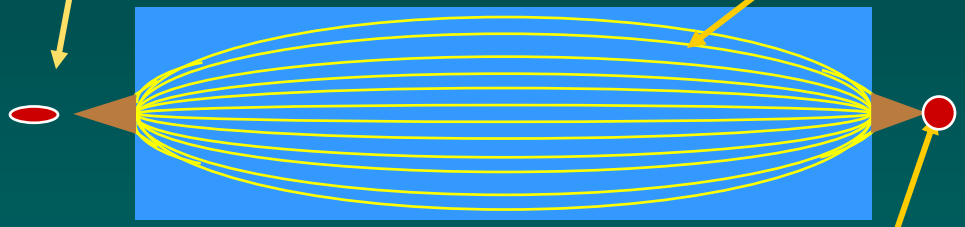


# Monolithic Polycapillary X-ray Optics

Polycapillary

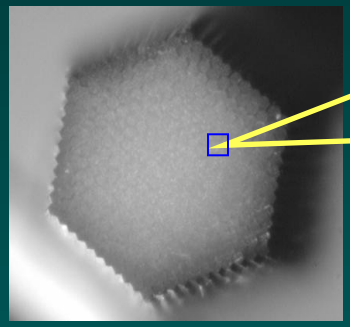
x-ray source

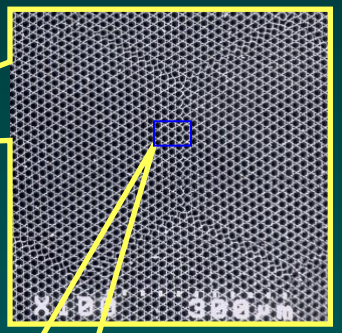
glass capillaries

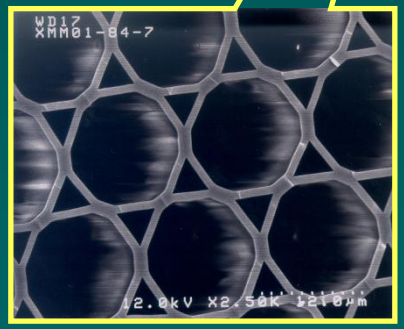


focal spot

Individual capillary




Los Alamos NATIONAL LABORATORY EST.1943

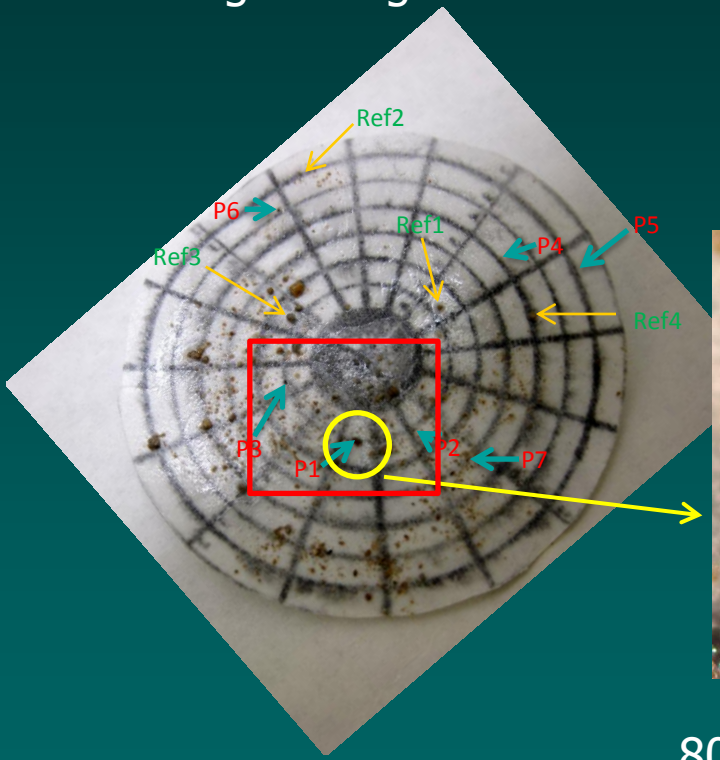
CHEMISTRY

NNSA

# EDAX Eagle III MXRF

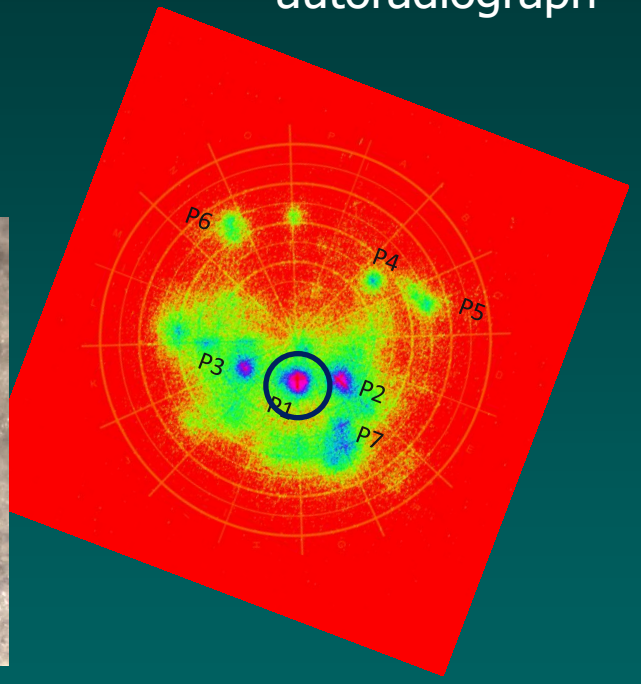
# Pu contaminated soil particles on filter

white light image



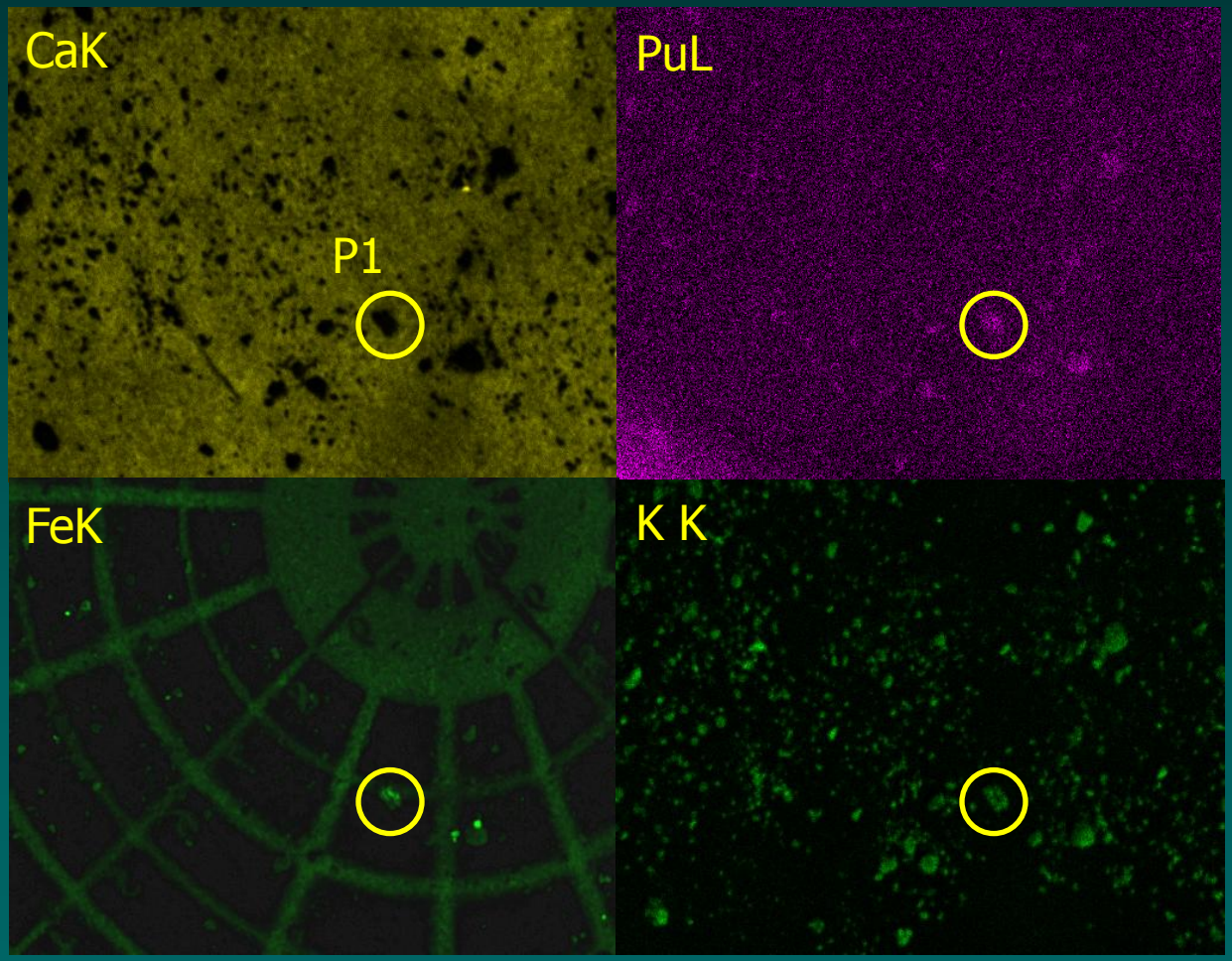

P1 - magnified white light image

autoradiograph

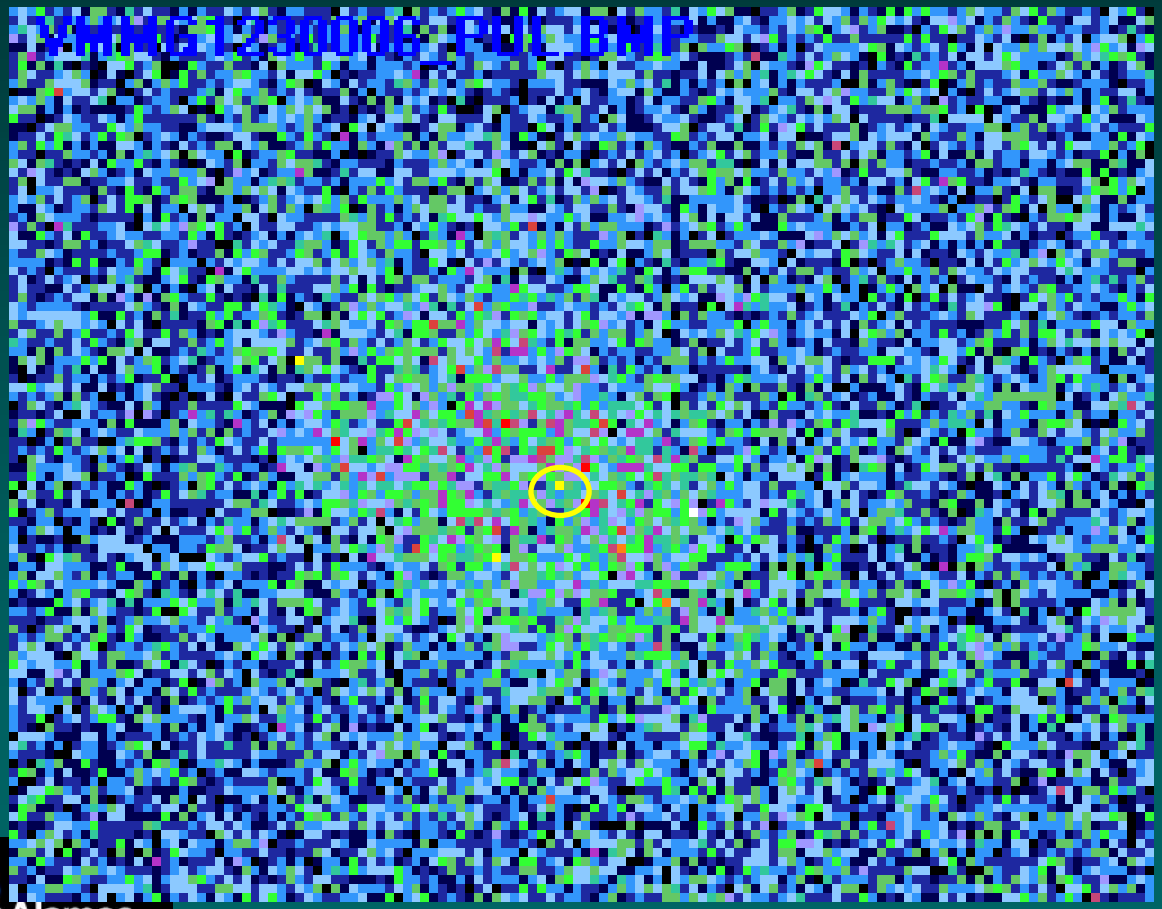



800 x 600 x 400 micrometers

# EDXRF Elemental Maps of Soil Particles on Filter

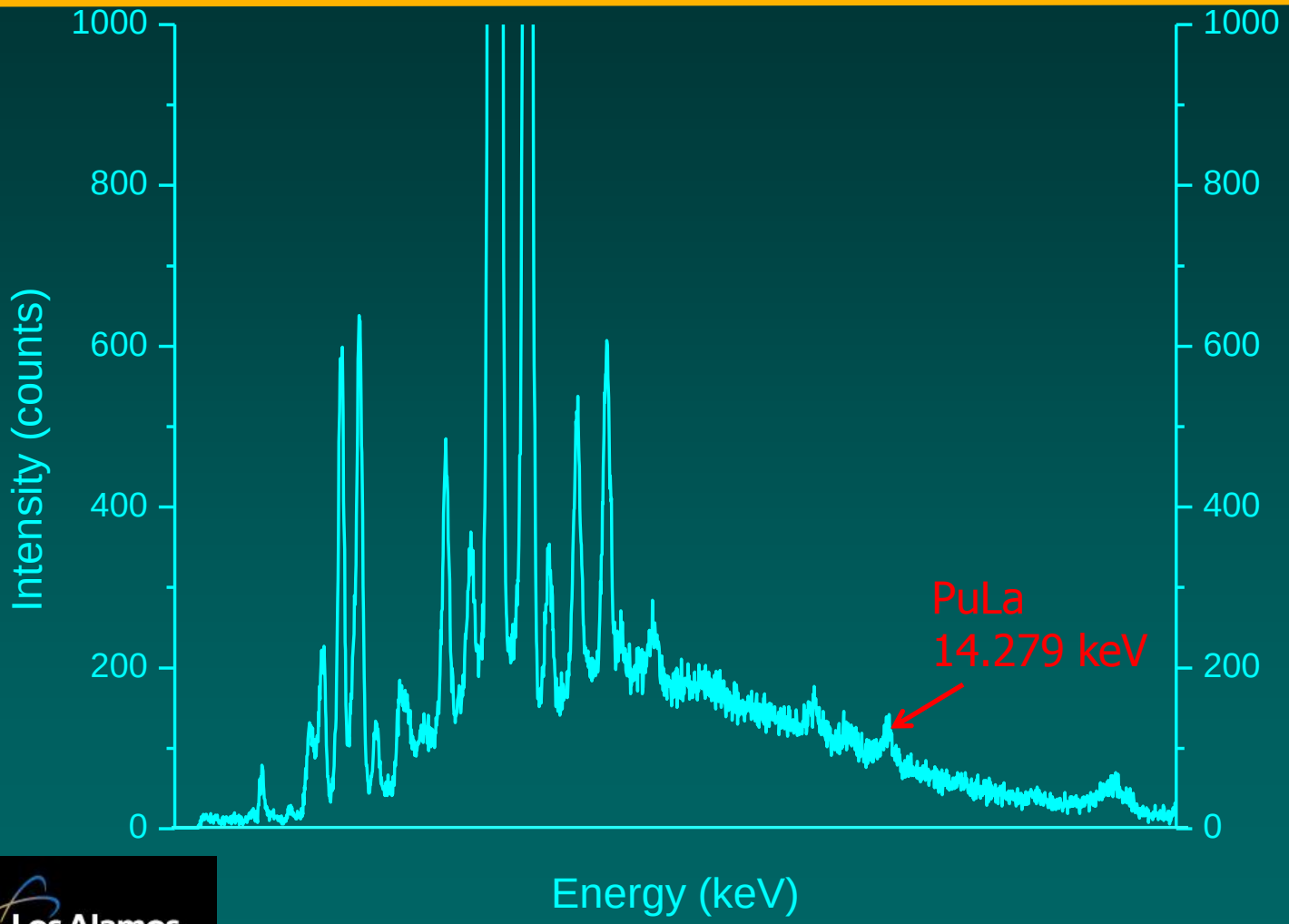


# EDXRF Pu map of P1 particle




50 micrometer spot size
200 ms dwell per point

# EDXRF spectra of P1 soil particle




187 ng Pu in particle

# MXRF

- Commercially available lab-based instrumentation
- Low power X-ray tube sources
- Vendor software for elemental mapping
- Good sensitivity and spatial resolution

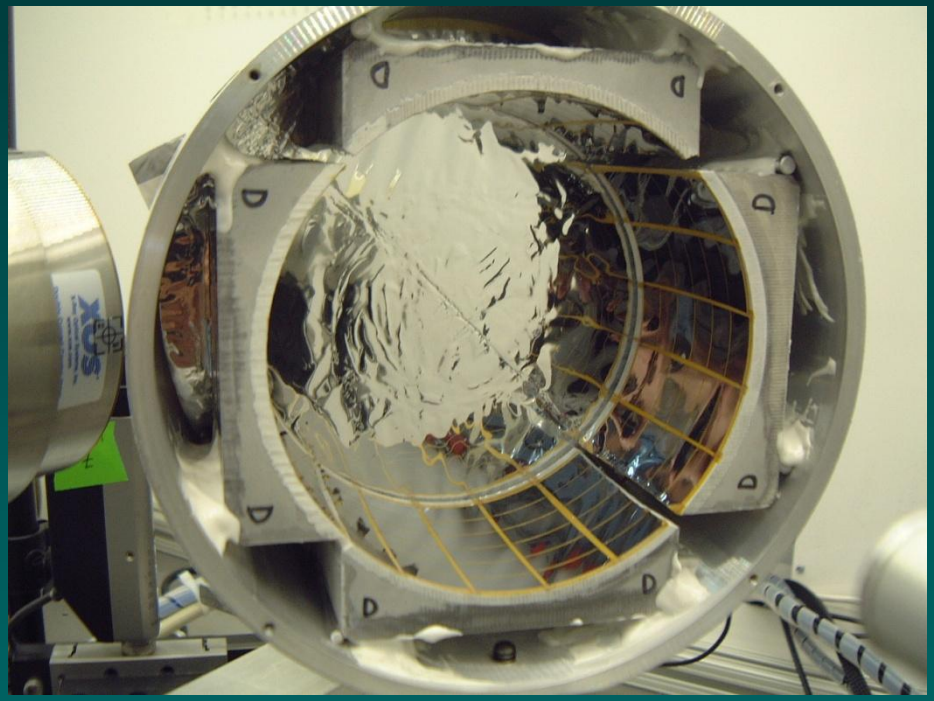
# hiRX

- high Resolution X-ray – based on MWDXRF technology developed for direct compositional characterization of spent nuclear fuel
- MWDXRF – (monochromatic wavelength dispersive XRF) utilizes doubly curved crystals (DCC) to focus and monochromatize the X-rays passing through the optic both for excitation and detection

# hiRX

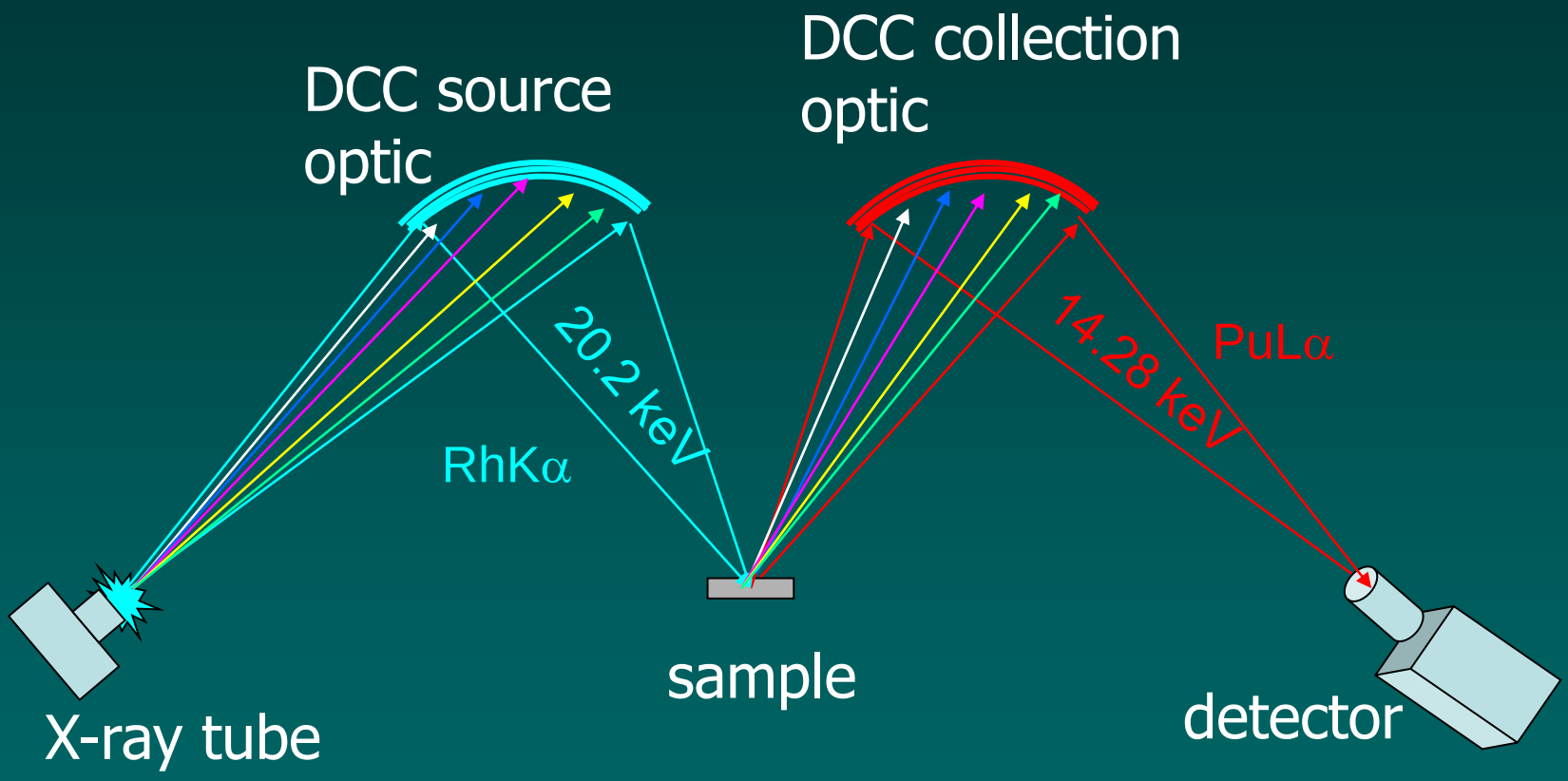
- DCC optics – focus and monochromatize X-rays Based on Bragg diffraction
  - Select both excitation and detection energies
- MWDXRF – monochromatic wavelength dispersive XRF
  - Monochromatic excitation using Rh Ka line 20.2 keV
  - Monochromatic detection – selected analyte target Pu at 14.28 keV

# DCC X-ray optics

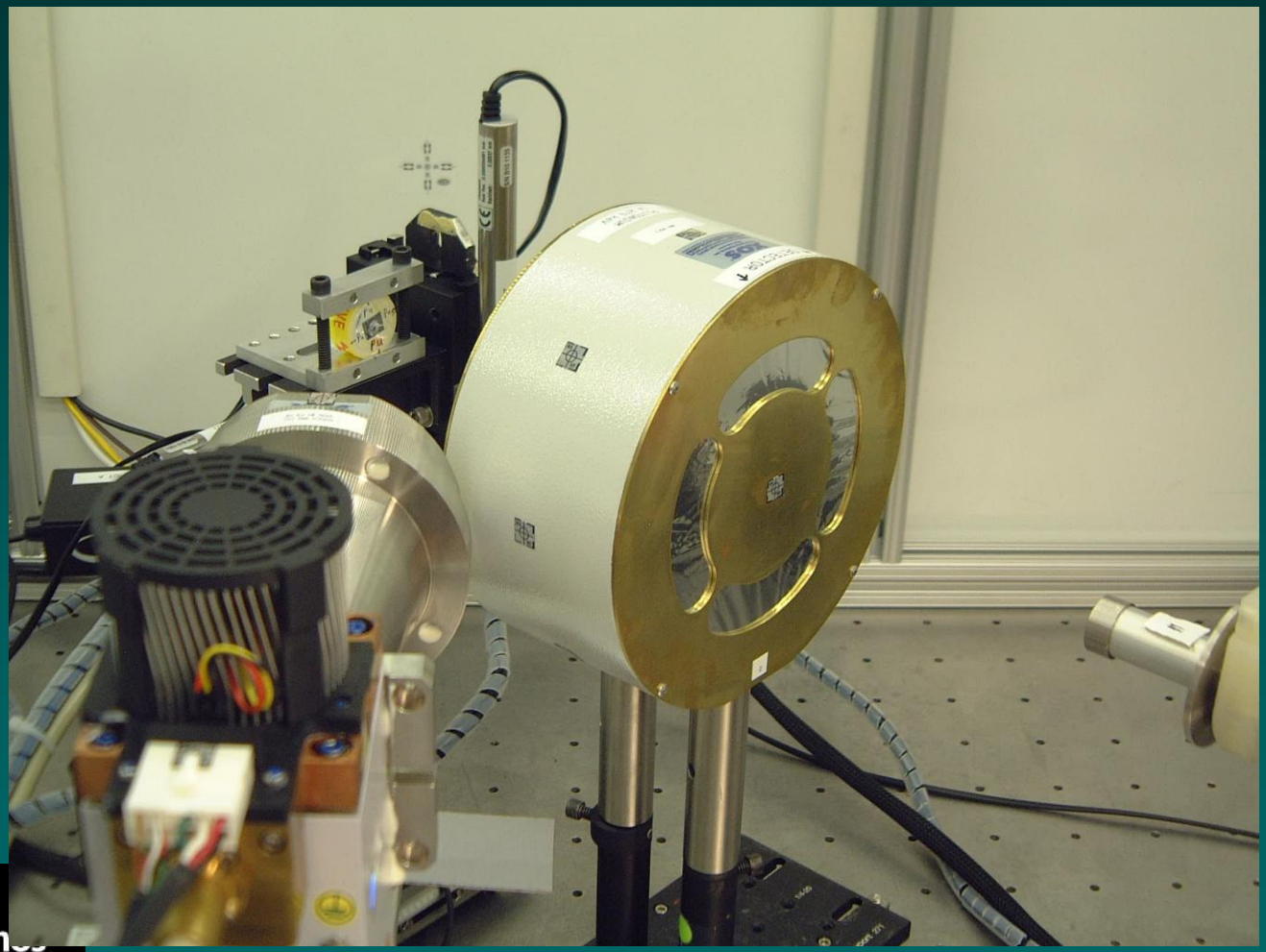


- Monochromatic optics
- Si, Ge, quartz, graphite or mica crystal material
- 10-20% reflectivity
- Useful for X-rays of energy 1.5 keV-35 keV

# hiRX Schematic Diagram



# hiRX Prototype Instrument



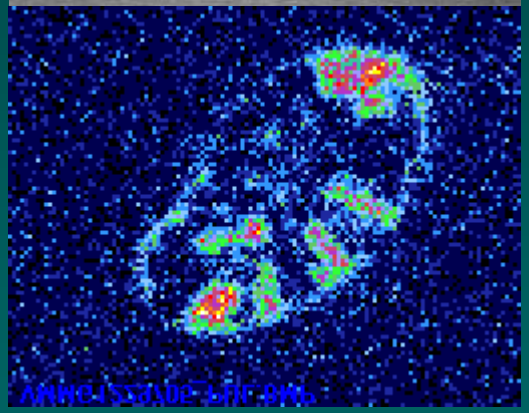
# hiRX Technology

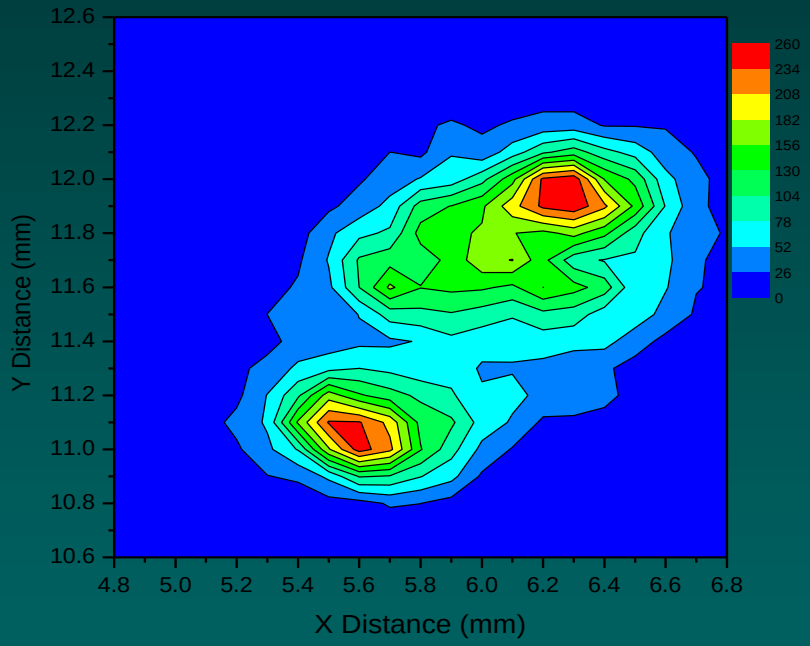
- Doubly curved crystal (DCC) optics for excitation and collection
- Small spot excitation – several hundred micrometers
- Small sample requirements – 1 microliter or less
- Collection optic to reject background and collect only analyte signal

# Simple matrix - Aqueous Pu Drop 270 μg Pu deposit

white light image of dried residue

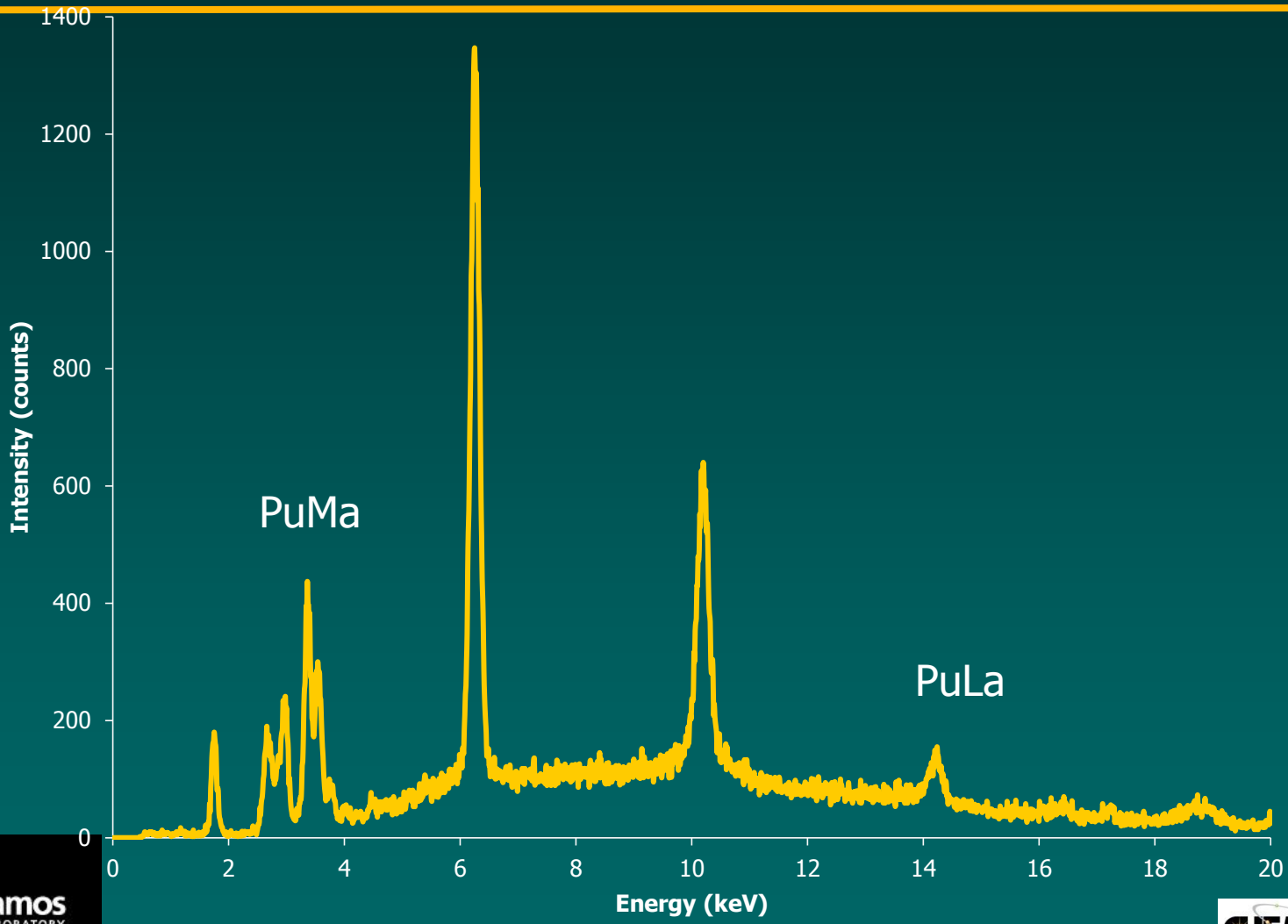
EDAX PuLa image with 50 μm spot size



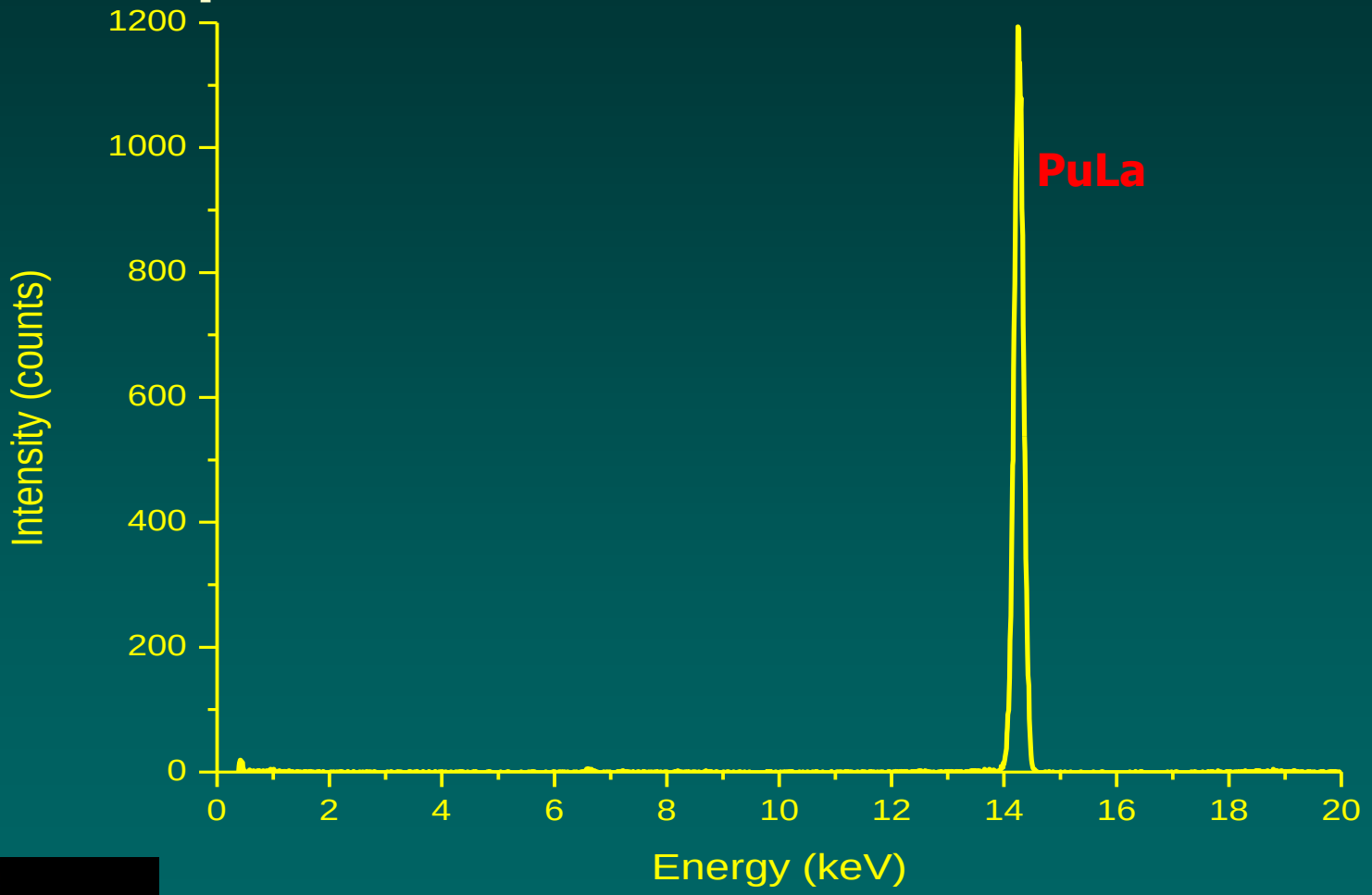



hiRX PuLa image with 200 μm spot size

# EDXRF spectrum Pu Drop #1

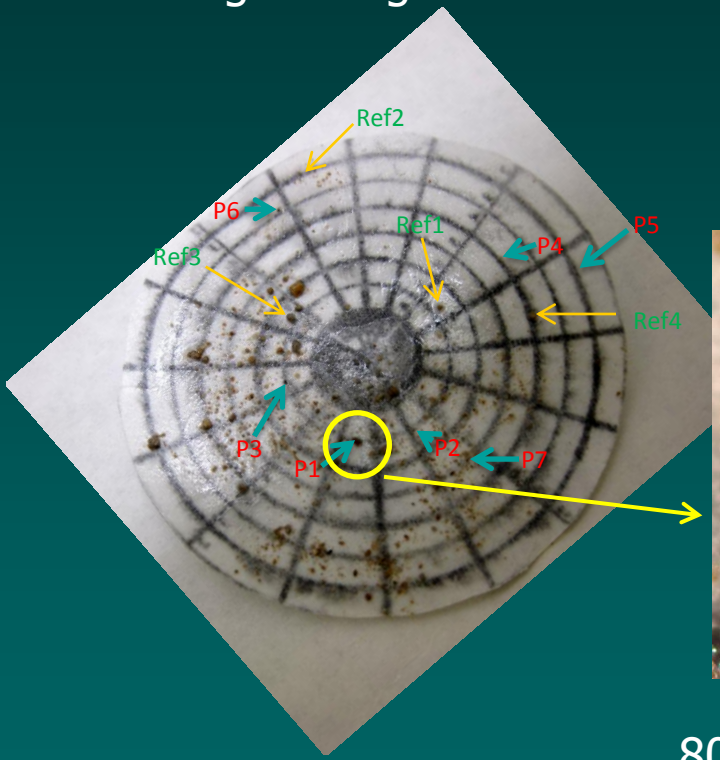


# hiRX spectrum of Pu Drop #1 hot spot



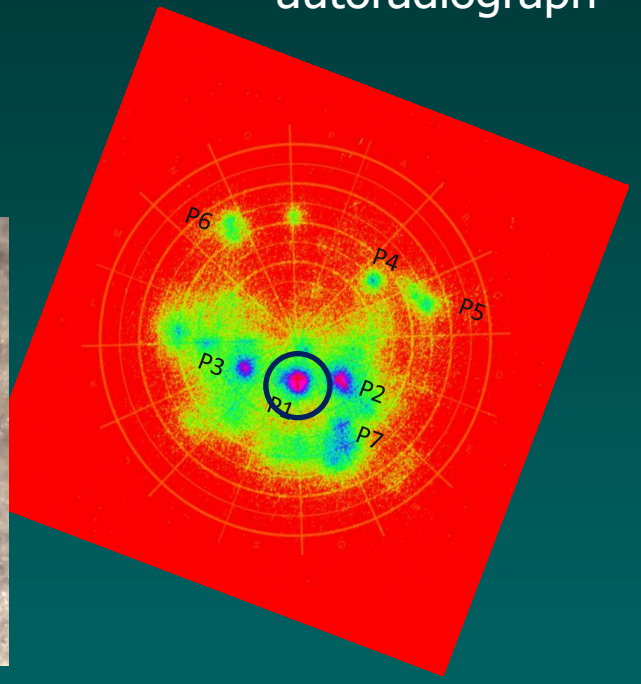
# Moderate matrix - Soil particles on filter

white light image




P1 - magnified white light image

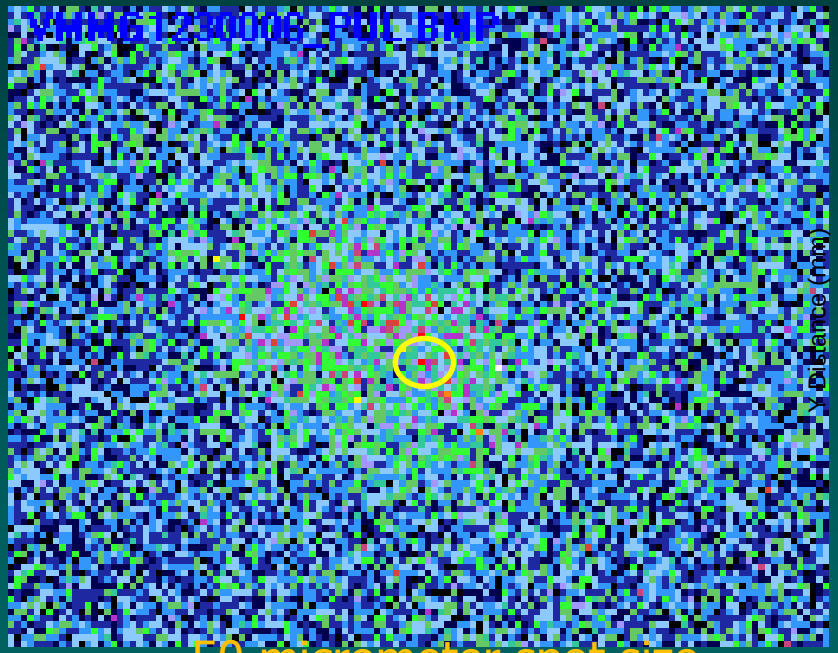
autoradiograph




800 x 600 x 400 micrometers

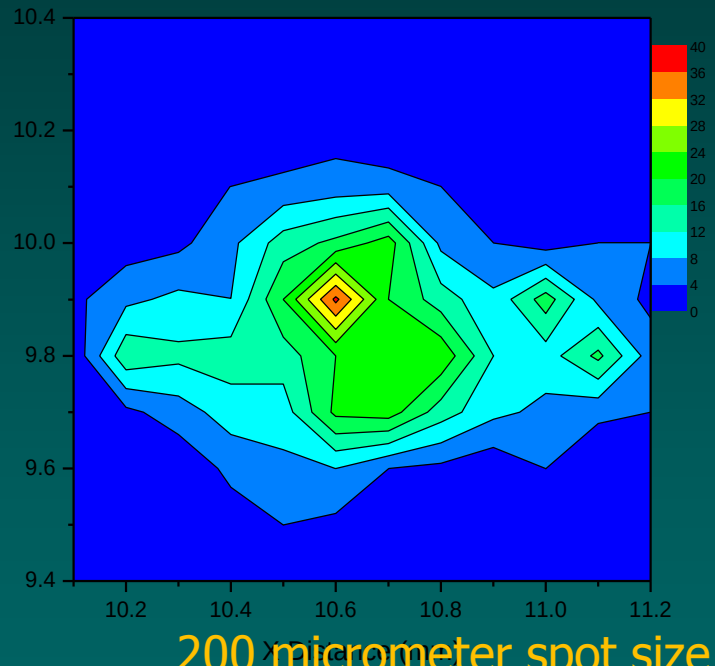
# EDXRF and hiRX Elemental Maps of P1

EDXRF



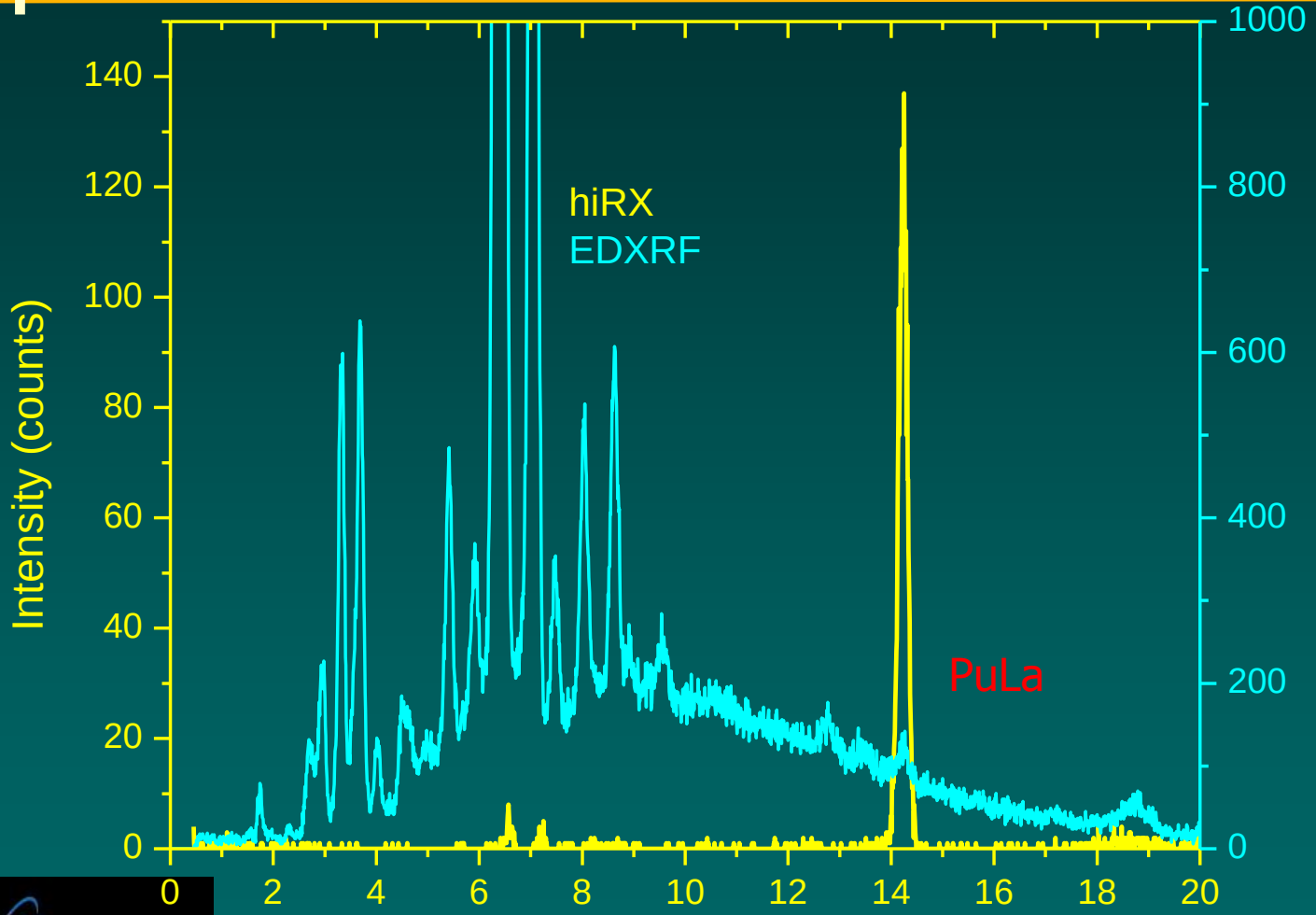
50 micrometer spot size
200 ms dwell per point

hiRX




200 micrometer spot size
3 s dwell per point

# hiRX-EDXRF spectra of P1 soil particle

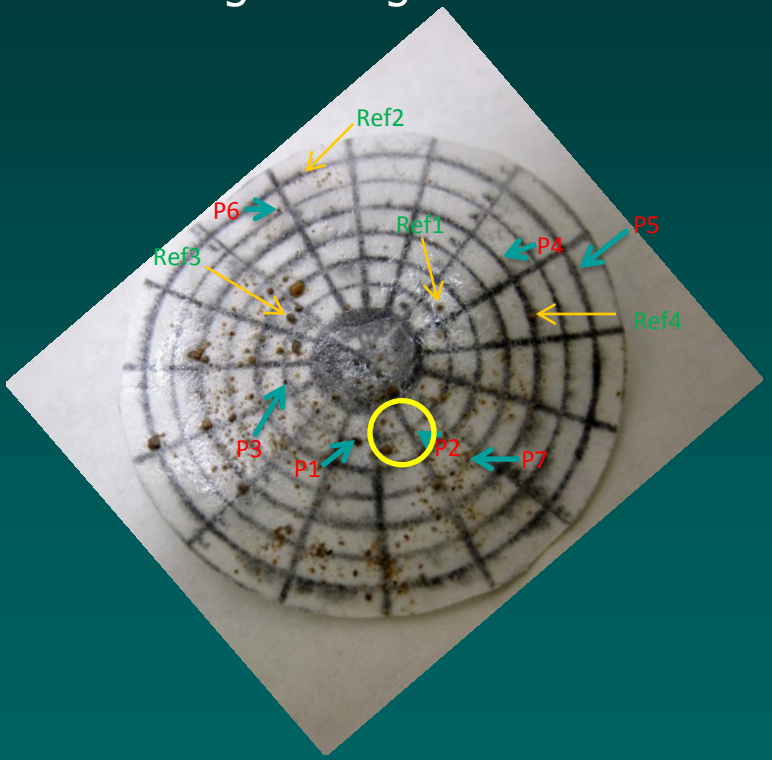



187 ng Pu in particle

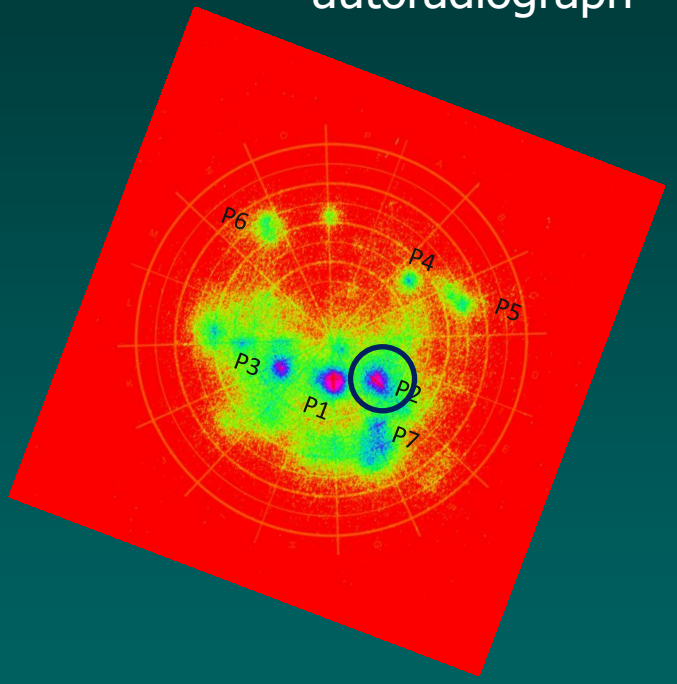
**Calculated LOD ~ 110 pg**

# Moderate matrix - Soil particles on filter P2

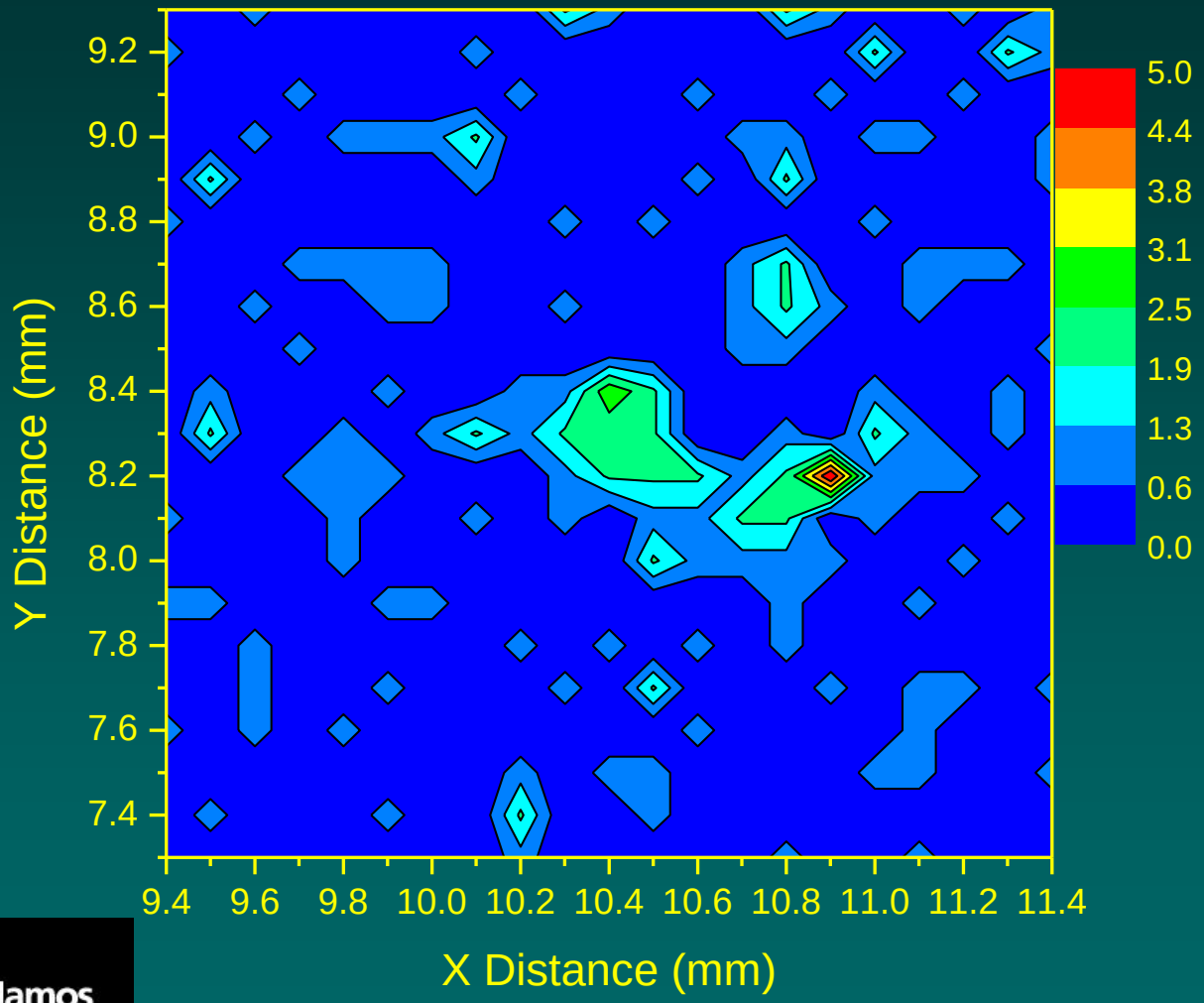
white light image



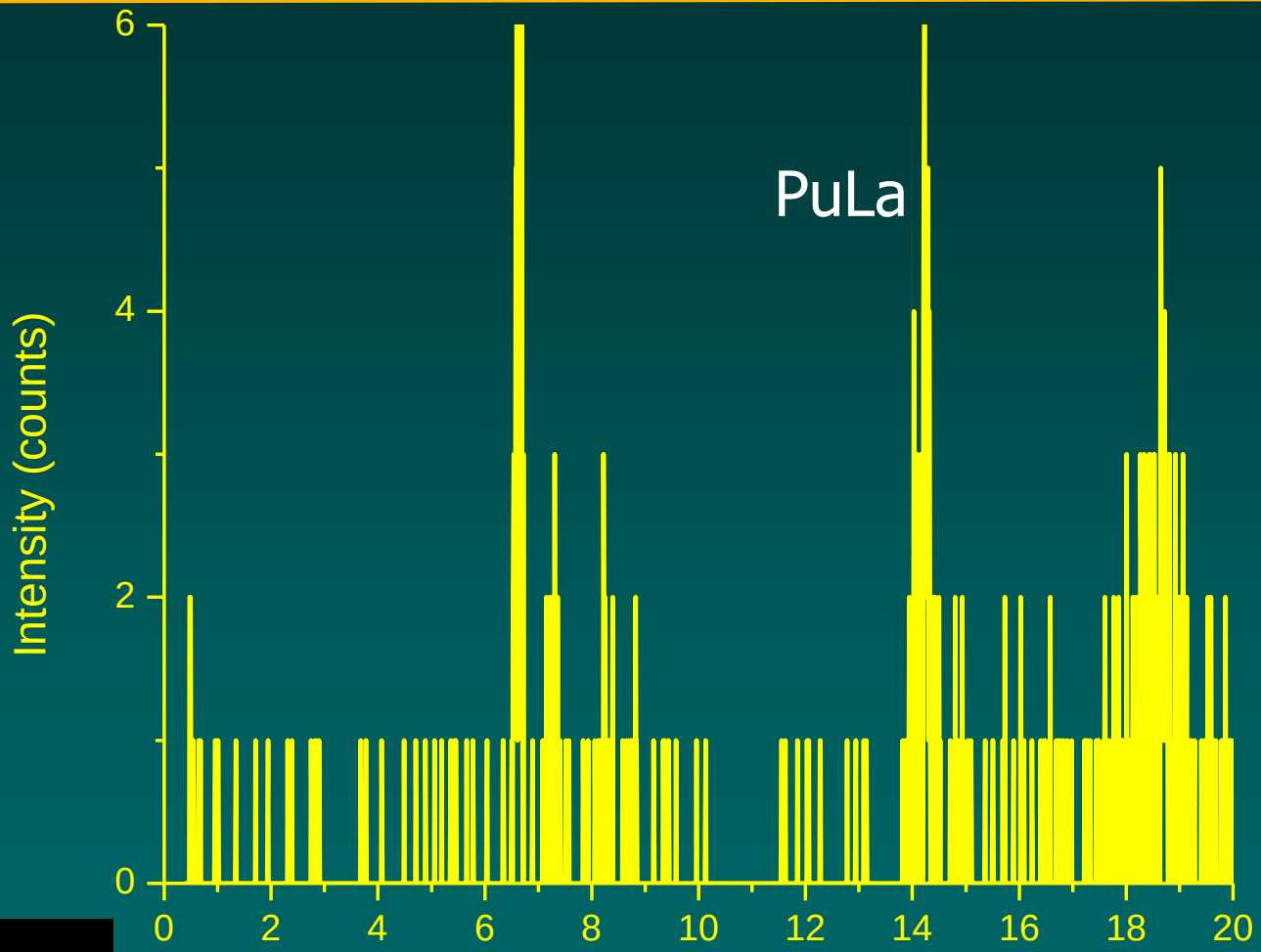

autoradiograph



# hiRX elemental map of P2 particle



# hiRX spectrum P2 particle




No EDXRF spectrum

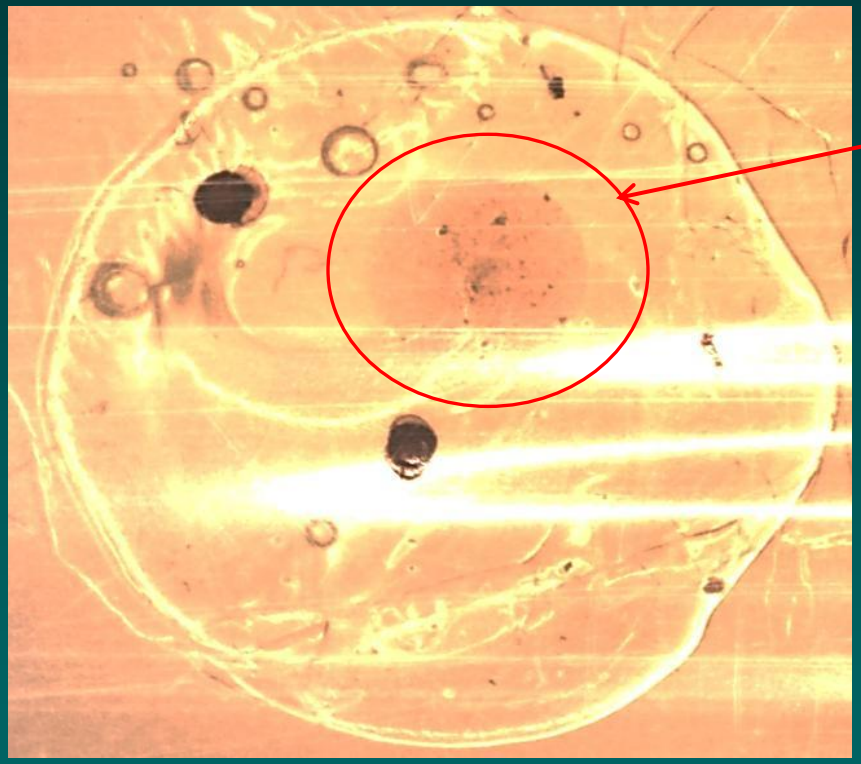
# Complex matrix – Spiked Synthetic Spent Fuel

| Element | X-Ray Energies | Element | X-Ray Energies |
|---|---|---|---|
| AgL | 2.98 | NiK | 7.47 |
| AsK | 10.54 | OsL | 8.91 |
| AuM | 2.12 | PdL | 2.83 |
| BaL | 4.46 | PrL | 5.03 |
| BiM | 2.42 | PtM | 2.05 |
| CdL | 3.13 | RbK | 13.39 |
| CeL | 4.84 | ReL | 8.65 |
| CsL | 4.28 | RhL | 2.69 |
| CuK | 8.04 | RuL | 2.55 |
| DyL | 6.49 | SbL | 3.6 |
| ErL | 6.94 | SeK | 11.22 |
| EuL | 5.84 | SmL | 5.63 |
| GaK | 9.25 | SnL | 3.44 |
| GdL | 6.05 | SrK | 14.16 |
| GeL | 1.18 | TaL | 8.14 |
| HfL | 7.89 | TaM | 1.71 |
| HoL | 6.72 | TbL | 6.25 |
| I L | 3.937 | TeL | 3.76 |
| InL | 3.28 | TmL | 7.18 |
| IrL | 9.17 | W L | 8.39 |
| LaL | 4.65 | W M | 1.775 |
| LuL | 7.65 | Y K | 14.95 |
| MnK | 5.89 | YbL | 7.41 |
| MoL | 2.29 | ZnK | 8.6 |
| NdL | 5.23 | ZrL | 2.04 |

nominal concentration of each element is 100 ng

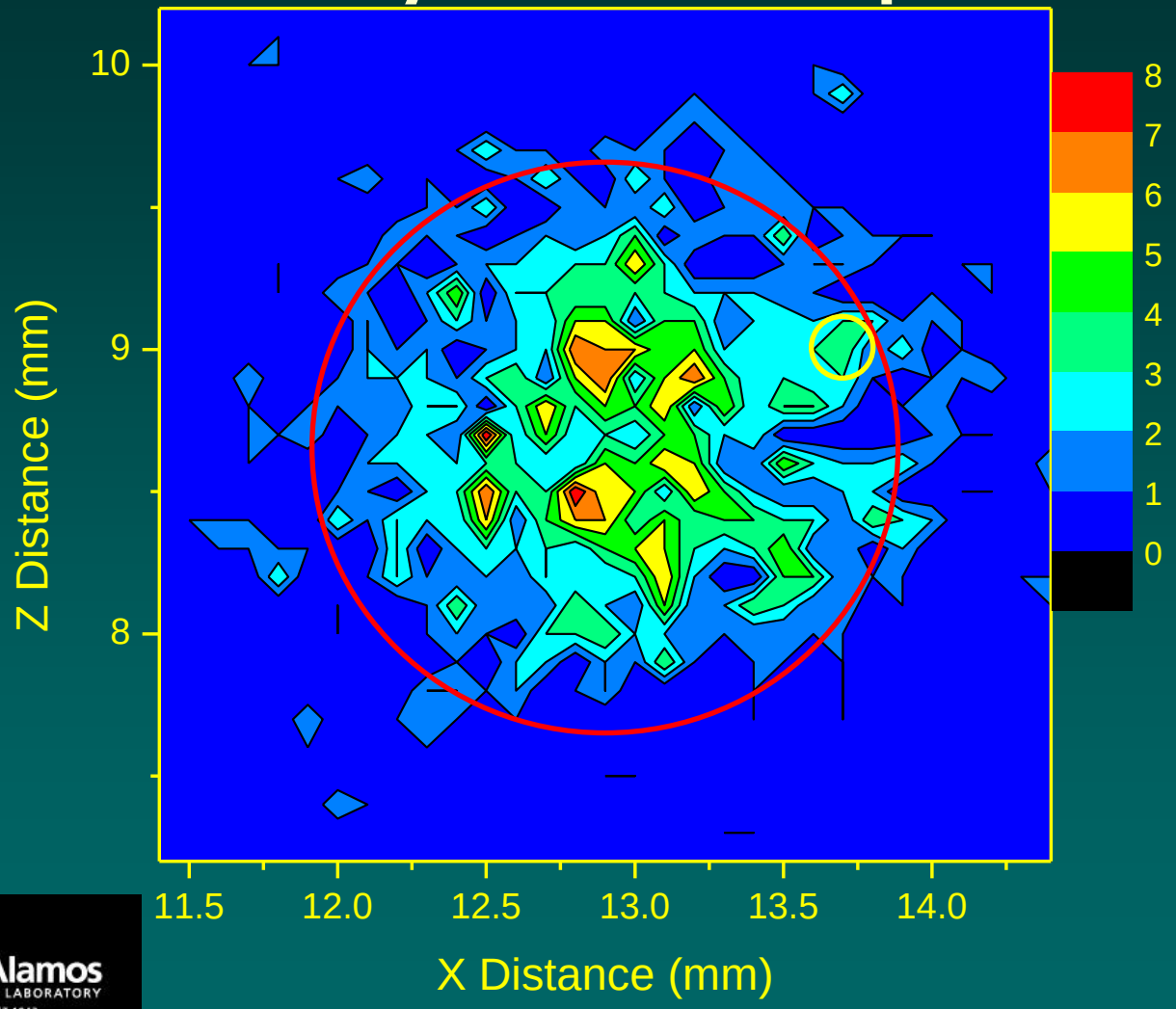
U is spiked at 10 μg
Pu at 30 ng

# Spiked Synthetic Spent Fuel



Spike deposit is ~1800 micrometers in diameter

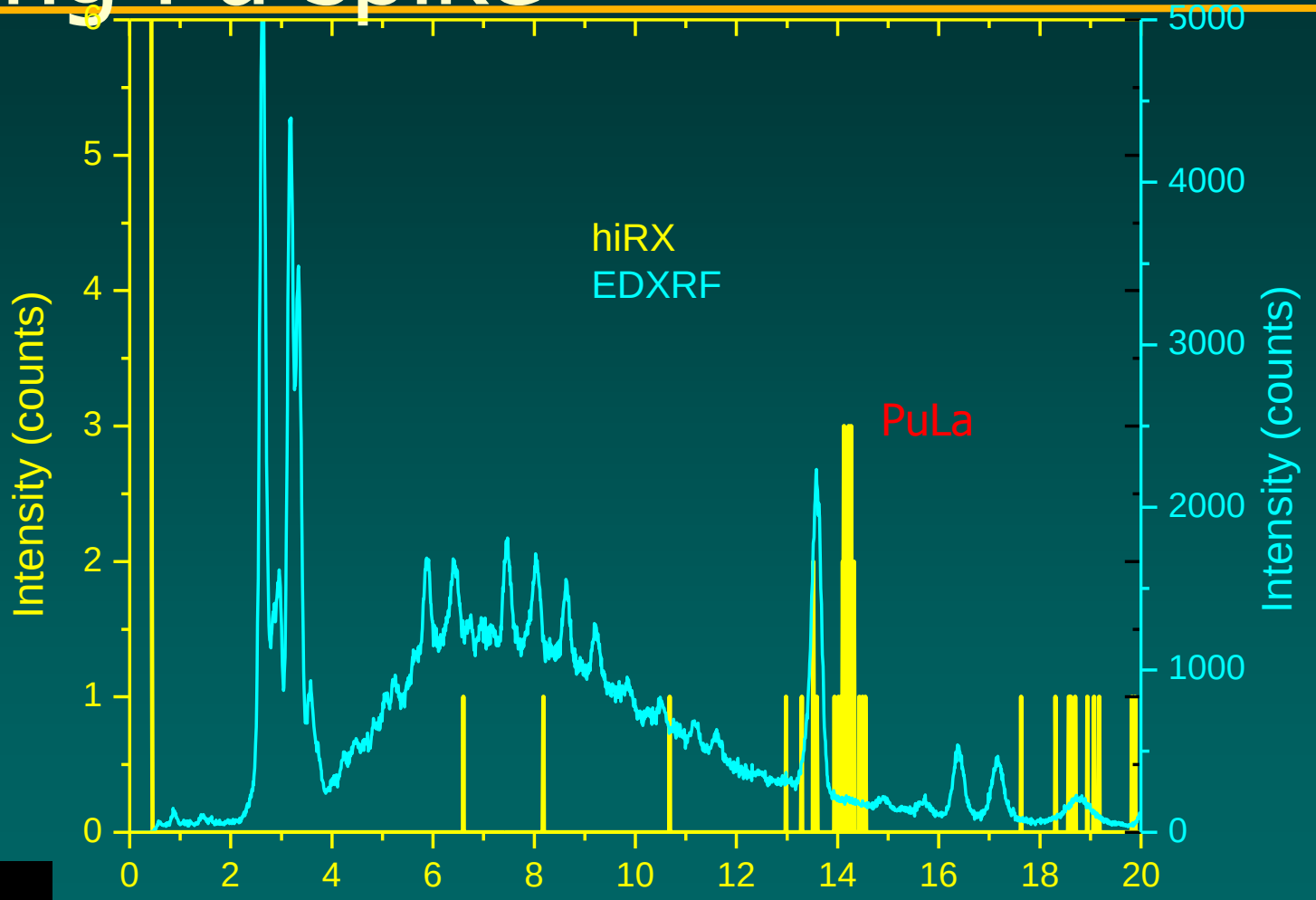
# hiRX elemental map of 30 ng Pu spike in synthetic spent fuel




Red ring – deposit diameter ~1800 micrometers

Yellow ring – excitation spot size diameter ~200 micrometers

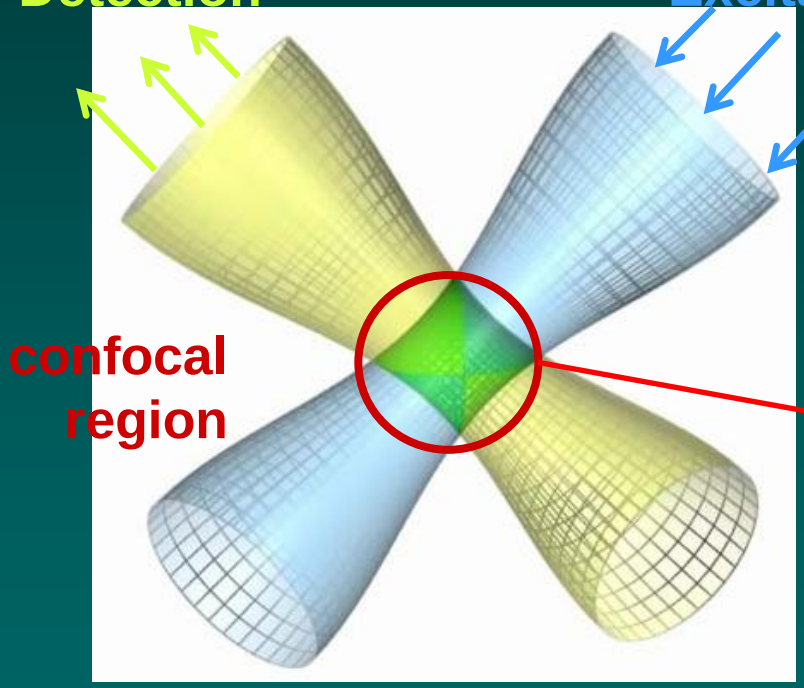
# Spectra overlay hiRX and EDXRF 30 ng Pu spike



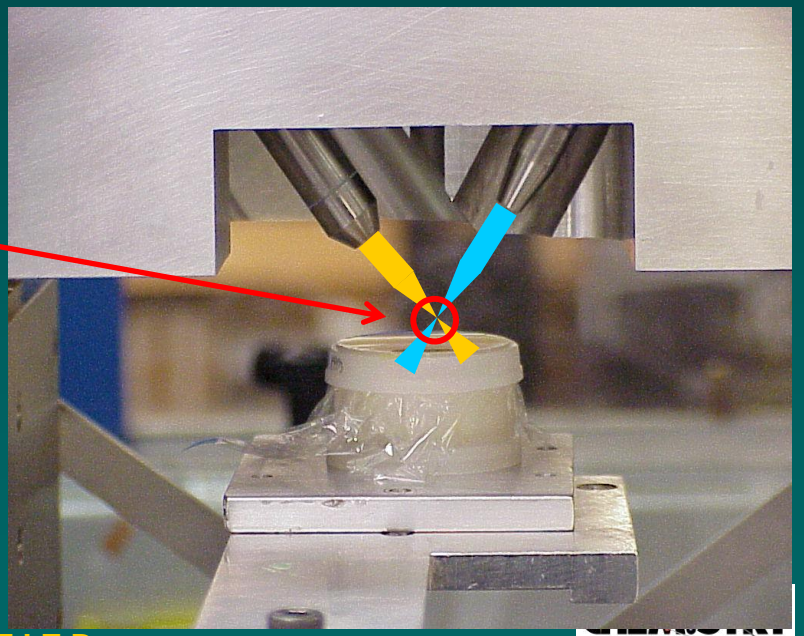
# DCC optics

- Monochromatic excitation – low background, high intensity
- Monochromatic collection/detection – high sensitivity, high selectivity
- Single element mapping

# Confocal Geometry




- overlap the two focal spots
- monolithic polycapillaries



# Confocal MXRF

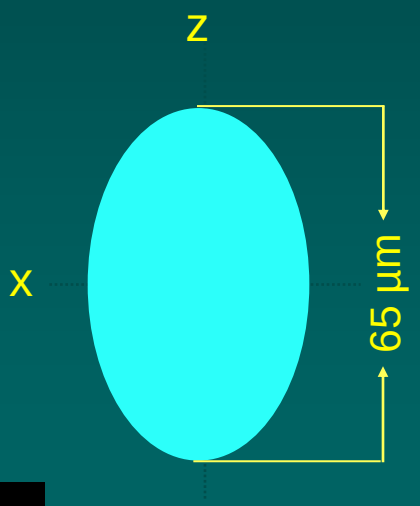
Beam dimensions at 30 kV, 0.3 mA

z: ~65 µm

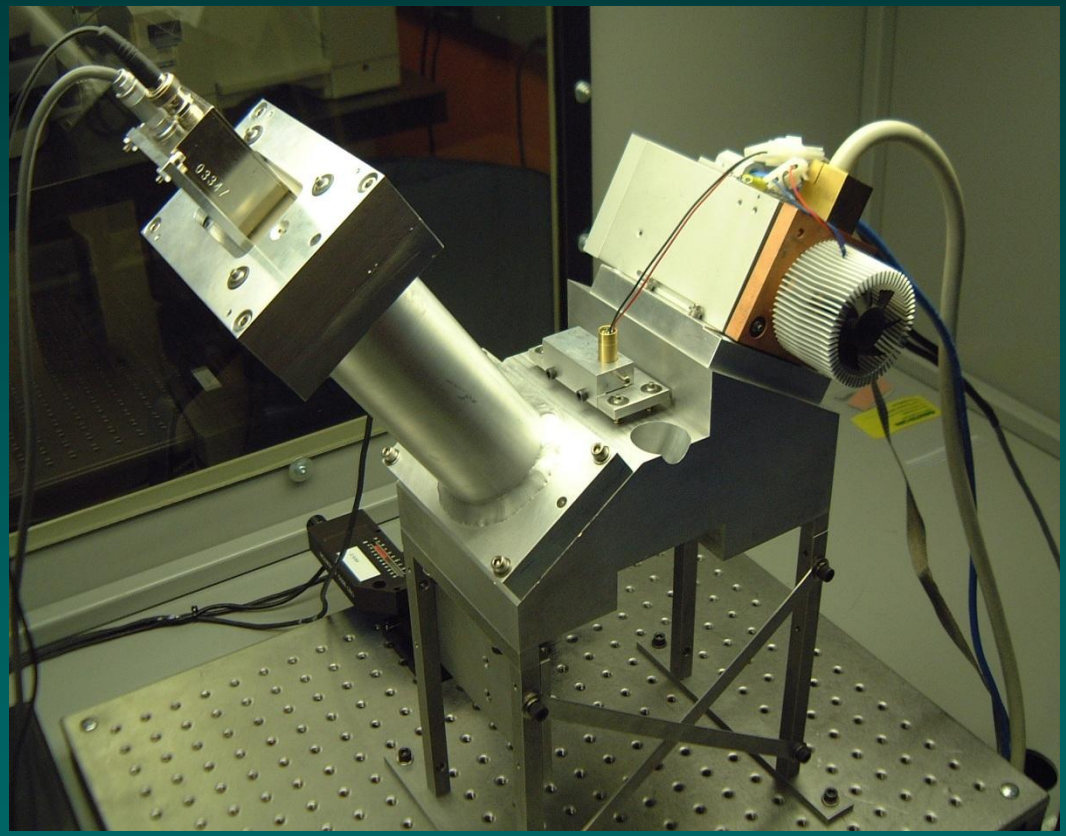
y: ~30 µm

x: ~30 µm

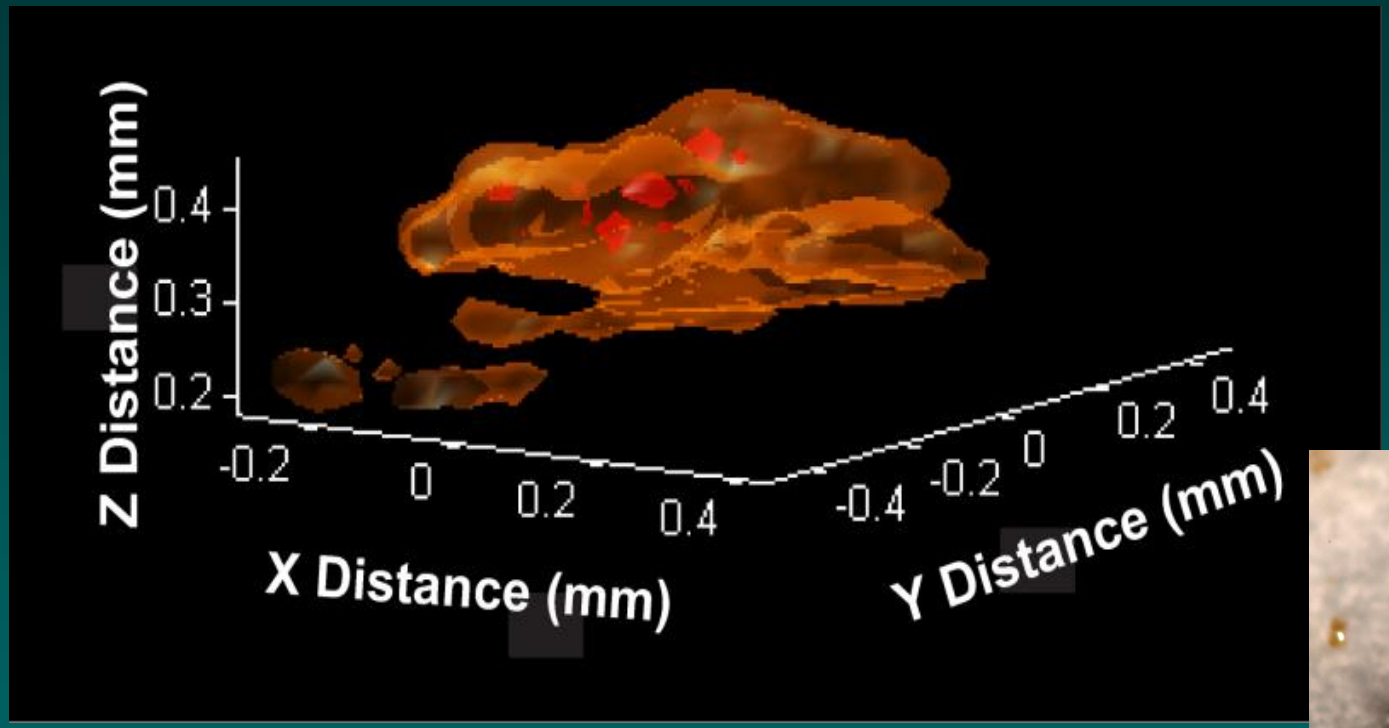
* Based on the first derivative *




beam is ellipsoidal



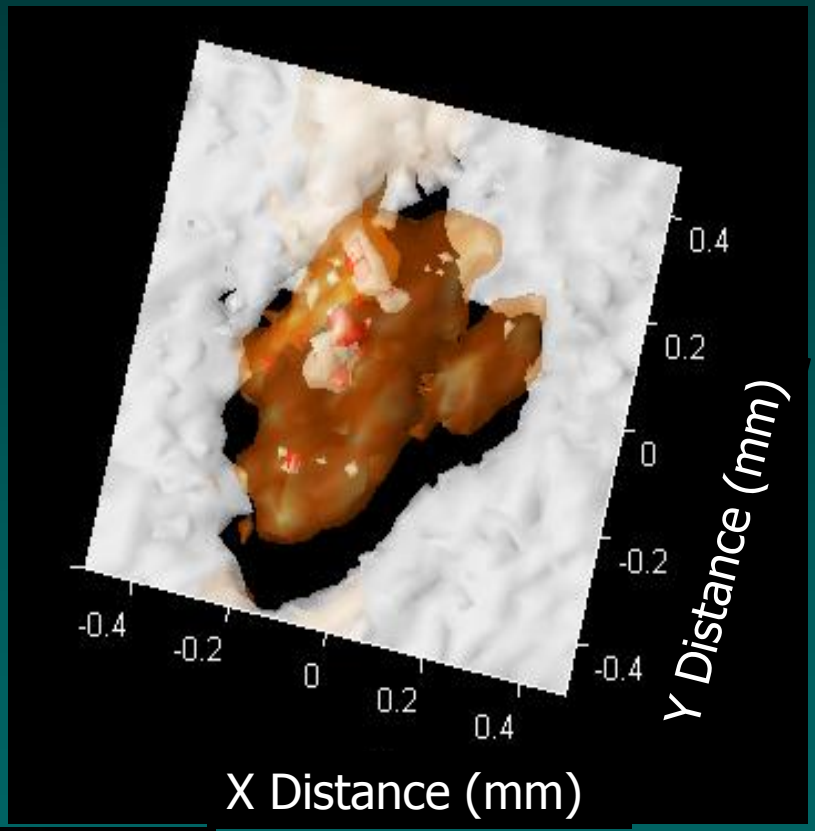
# 3D Image of Pu P1 Particle



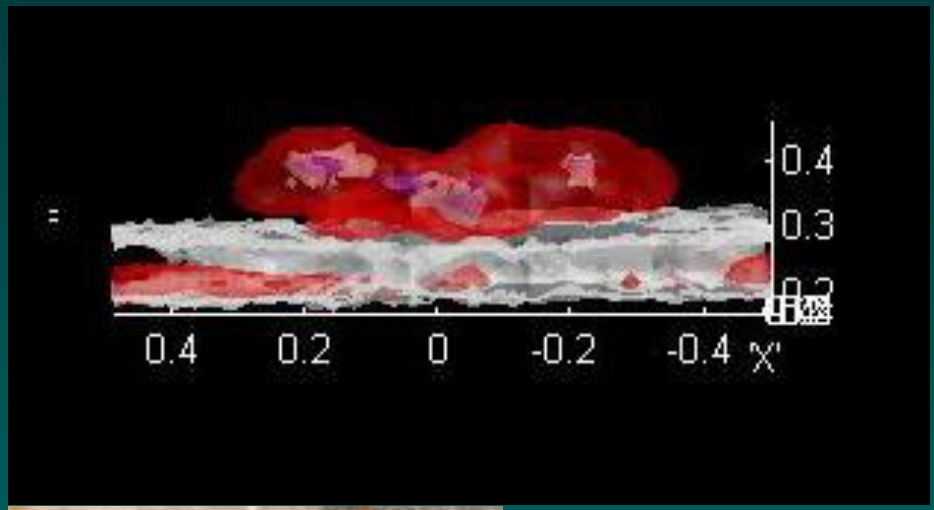

orange - Fe
red – Pu

# Confocal 3D images P1 particle

Top view




Side view




# Confocal

- 3D nondestructive elemental imaging
- Depth penetration from 10's to 1000's of micrometers depending upon analyte and matrix
- Multi-element depth dependent imaging
- Unique elemental characterization technique

# Optic Comparison

| | Polycapillary | DCC | Monocapillary | Aperture |
|---|---|---|---|---|
| Smallest Spatial Resolution | | | ✓ | |
| Highest Flux (cps) | | ✓ | | |
| Highest Flux Density (cps/area) | ✓ | | | |
| Fastest Data Acquisition | ✓ | | | |
| Lowest Detection Limits | | ✓ | | |

# Applications

- Catalysts before and after use
- Fossil visualization
- Bone and tissue mapping
- Meteorite composition
- Minerals
- Photovoltaics, batteries, fuel cells
- Integrated spectrometry with Raman and FTIR

# Summary

- X-ray optics provide unique capabilities for spatially resolved nondestructive elemental analyses
- No one optic provides complete capabilities of spatial resolution, energy transmission and sensitivity
- Focus on laboratory based instrumentation, for MXRF

# Summary

- Select appropriate X-ray optics to optimize data acquisition
- Polycapillary offers good spatial resolution, limited by energy filtering
- hiRX DCC offers highest sensitivity, limited to single element detection

# Acknowledgements


- The support of the Next Generation Safeguards Initiative (NGSI), Office of Nonproliferation and International Security (NIS), National Nuclear Security Administration (NNSA).
- Velma Montoya
- Christopher Galvin
- Hakim Boukhalfa
- Michael Collins